IMPROVED REFRACTORY MATERIALS FOR SLAGGING GASIFIERS IN IGCC POWER SYSTEMS

James P. Bennett
U.S. Department of Energy Albany Research Center, 1450 Queen Ave., SW, Albany, OR 97321
E-mail: jbennett@alrc.doe.gov; Telephone: (541) 967-5983; Fax: (541) 967-5845

Kyei-Sing Kwong, Cynthia Powell, Rick Krabbe, and Hugh Thomas
U.S. Department of Energy Albany Research Center, 1450 Queen Ave., SW, Albany, OR 97321

ABSTRACT

Gasifiers are the heart of Integrated Gasification Combined Cycle (IGCC) power system currently being developed as part of the DOE's Vision 21 Fossil Fuel Power Plant. A gasification chamber is a high pressure/high temperature reaction vessel used to contain a mixture of O_2, H_2O, and coal (or other carbon-containing materials) while it is converted into thermal energy and chemicals (H_2, CO, and CH_4). IGCC systems are expected to play a dominant role in meeting the Nation's future energy needs. Gasifiers are also used to produce chemicals that serve as feedstock for other industrial processes, and are considered a potential source of H_2 in applications such as fuel cells. A distinct advantage of gasifiers is their ability to meet or exceed current and anticipated future environmental emission regulations. Also, because gasification systems are part of a closed circuit, gasifiers are considered process ready to capture CO_2 emissions for reuse or processing should that become necessary or economically feasible in the future.

The service life of refractory liners for gasifiers has been identified by users as a critical barrier to IGCC system economics and to gasifier reliability and on-line availability. The refractory lining contains the harsh, high temperature/pressure gaseous environment, an environment that includes molten slag originating from impurities in the carbon source. The molten slag flows over the refractory surface and penetrates it, causing refractory dissolution in the slag and setting up the environment for refractory spalling to occur, the two primary wear mechanisms of refractories. The current generation of refractory liners need to be replaced within 3 to 24 months because of these wear mechanisms. Slag wear of a refractory lining by dissolution is highly dependent on gasifier feedstock, material throughput, gasification temperature, downtime frequency, and system maintenance. Spalling wear of a refractory is influenced by slag penetration depth, gasifier cycling, and rapid temperature changes; and leads to small portions of a liner peeling from the working face lining. Predicting when a refractory lining needs replacement is difficult, with the cost of replacing all or part of the lining exceeding $1M, depending on the extent of the necessary repair/replacement. Compounding material and installation costs are lost opportunity costs that occur when a gasifier is off-line for refractory replacement or repair. Industry would like refractory materials that have a predictable and improved service life of 50 pct. ARC's program goal is to attain improved service life and reliability in refractory liners through materials research.

To improve refractory service life, ARC scientists have developed and patented a high chrome oxide, phosphate containing, refractory composition. This material has excellent slag penetration resistance properties in laboratory testing, was commercially produced by a refractory manufacturer, has been installed in a commercial coal slagging gasifier, and is undergoing field trials. An expansion of field trials is underway through discussions with several gasifier operators because of large variations in gasifier operation and carbon feedstocks, with testing of the phosphate containing refractory material planned in systems using petroleum coke and coal/petroleum coke carbon feedstock. These plant trials

will indicate if a service life improvement occurs in the newly developed material, or if further modifications of the composition are needed.

Research is also underway at ARC to develop no chrome or low chrome oxide refractory materials, refractories not actively considered for gasifier use since the mid 70's to 80's, when early research indicated high chrome oxide materials had superior performance to all other refractory materials tested. Since that time, significant improvements in refractory technology, new raw materials, and a greater understanding of gasifier wear mechanisms may make it possible to engineer the development of better no- or low-chrome oxide liner materials. Some driving forces for this research are because chrome oxide refractories: a) have not met the service life requirements, b) have a high cost, c) have a high density (creating weight, size and joint issues), d) have possible long term supply issues, e) have perceived/real safety concerns, and f) have limited repair options and cause lengthy repair turnaround. Albany is researching new materials that include Al_2O_3, MgO, ZrO_2, MgO/Al_2O_3 spinels, or engineered combinations of them for potential use as hot face liners.

Results of research to develop an improved high chrome oxide refractory material and of efforts to develop no/low chrome oxide materials will be presented.

INTRODUCTION

Gasifiers are the heart of Integrated Gasification Combined Cycle (IGCC) power system currently being developed as part of the DOE's Vision 21 Fossil Fuel Power Plant. Gasifiers are also used to produce chemicals that serve as feedstock for other industrial processes, and are considered a potential source of H_2 in applications such as fuel cells. An IGCC gasification chamber is a high pressure/high temperature reaction vessel used to contain a mixture of O_2, H_2O, and coal (or other carbon-containing materials) while it is converted into thermal energy and chemicals (H_2, CO, and CH_4). In a slagging gasifier, the reaction chamber operates at temperatures between about 1250º-1550ºC, at pressures up to 1000 psi, and is lined with refractory materials to contain the severe environment and to protect the outer steel shell from erosion, corrosion, and temperature. An example of an IGCC gasification system with an air cooled slagging gasifier is shown in Figure 1. IGCC systems are expected to play a dominant role in meeting the Nation's future energy needs. A distinct advantage of gasifiers is their ability to meet or exceed current and anticipated future environmental emission regulations. Also, because gasification systems are part of a closed circuit, gasifiers are considered process ready to capture CO_2 emissions for reuse or processing should that become necessary or economically feasible in the future.

The service life of refractory liners for slagging gasifiers has been identified by users as a critical barrier to IGCC system economics and to gasifier reliability and on-line availability[1]. The refractory lining contains the harsh, high temperature/pressure gaseous environment, an environment that includes molten slag originating from impurities in the carbon source. Coal, petroleum coke, and mixtures of them are the primary carbon sources, although other materials such as biomass waste and black liquor are also being explored as carbon feedstock.

Refractory liners for slagging gasifiers are typically of two types; high chromia-alumina and high chromia-alumina-zirconia, with historical use of chromia-magnesia linings. The use of high chromia refractories evolved from gasifier research in the mid 70's to 80's, which indicated high chromia content in a refractory (75 wt pct or higher) gave superior performance to all other refractory materials tested[2]. Since that time, significant improvements in refractory technology, new raw materials, and a greater understanding of gasifier wear mechanisms may make it possible to engineer the development of better no- or low-chrome oxide liner materials. Driving forces for no/low chrome oxide research are because chrome oxide refractories: a) have not met the service life requirements, b) have a high cost, c) have a high density (creating weight, size and joint issues), d) have possible long term supply issues, e) have perceived/real safety concerns, and f) have limited repair options and cause lengthy repair turnaround.

Molten slag from ash in the carbon source flows over the refractory surface in the gasifier and penetrates it, causing refractory dissolution in the slag, and setting up the environment for refractory spalling to occur. Whenever the carbon source is changed, slag attack of the refractory will be impacted due to changes in the ash chemistry. Refractory dissolution and spalling brought about by the slag and are thought to be the two primary wear mechanisms of refractory liners.

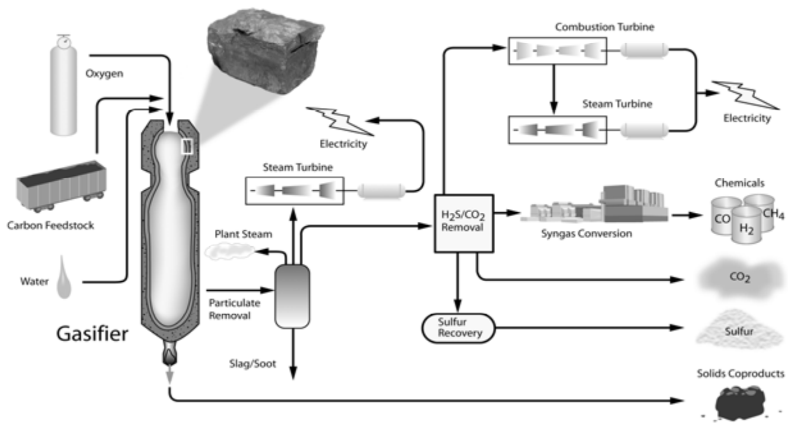

Fig. 1: Integrated Gasification Combined Cycle gasification system.

The current generation of refractory liners used in a gasifier must be replaced within 3 to 24 months of installation, depending on location in a gasifier, because of wear. Refractory wear by dissolution is highly dependent on gasifier feedstock, material throughput, gasification temperature, usage time, and system maintenance. Wear by spalling is influenced by slag composition and penetration depth, gasifier cycling, and rapid temperature changes; and leads to portions of a liner peeling from the working face lining.

Predicting when a refractory lining needs replacement is difficult, with the cost of replacing all or part of the lining exceeding $1M, depending on the extent of the necessary repairs. Compounding material and installation costs are lost opportunity costs that occur when a gasifier is off-line for refractory replacement or repair. Re-lining a gasifier requires that the system be completely shut down, and under the best of circumstances takes about 12 days; involving cool down (5-7 days) and teardown and repairs for a partial reline (3 days) or a full reline (7-10 days). Industry would like refractory materials that have a predictable and improved service life of 50 pct.

ARC's program goal is to attain improved service life and reliability in refractory liners through materials research. This paper discusses its research efforts to develop improved high chrome oxide refractory material and no/low chrome oxide material for slagging gasifiers.

CURRENT STATUS OF RESEARCH

CHROME OXIDE CONTAINING REFRACTORIES

The Albany Research Center has conducted post-mortem analysis of high chrome oxide spent refractory materials removed from slagging gasifiers and determined that the primary cause of material failure is caused by two factors: 1) dissolution of the refractory into the molten slag, and 2) spalling caused by slag penetration into the porous refractory material. Spalling is exuberated by cycling of the gasifier, and causes large portions of the hot face refractory to be incrementally removed, rapidly shortening refractory service life as large pieces of material are physically removed versus a slow material dissolution in slag[2].

The strategy taken at Albany to develop improved performance high chrome oxide refractory materials was by limiting slag penetration in the refractory, with the end result limiting /reducing spalling and corrosion (dissolution). Examples of spalling and dissolution as causes of refractory failure are shown in figure 2. Spalling in the process of occurring on the surface of a refractory sample removed from a gasifier is shown in figure 3.

Fig. 2: Flowing slag causing chemical dissolution of refractory sidewall and spalled refractory material (circled fragment).

Fig. 3: Refractory surface in the process of spalling (yellow arrows).

Phosphate additions were made by Albany to a high chrome oxide material, determined to reduce slag penetration, and patented (US patent No. 6,815,386). This refractory composition is being commercially produced, and is currently undergoing testing at in a commercial gasifier using coal as a feedstock. Previous testing at this gasifier was for 17 days, a test that was of limited duration, and was terminated for non-refractory reasons. The appearance of the test panel in service for 17 days appeared to have performance as good as or better than the currently used high chrome oxide refractory materials. Because of this performance, the decision was jointly made between the gasifier user and Albany to expand testing into the sidewall test area and to do a retest in the future in the lower cone area of the gasifier. Additional field test samples were made by the refractory company. The sidewall test samples were installed and put in service by the gasifier user, with installation of the lower cone materials waiting for a future tearout before being installed. The sidewall test panel containing the phosphate high chrome oxide materials has been in service for over 110 days. Test material currently undergoing evaluation as a sidewall panel is shown in figure 4.

Fig. 4: Sidewall test panel undergoing testing in a commercial gasifier. Refractory samples marked with red dots are test materials. Yellow dots are the traditionally used refractory materials.

When the gasifier with the test panel comes down for repair, samples of the test refractory will be evaluated for their performance compared to the traditionally used high chrome oxide refractory materials. No indication of high wear or premature failure has been noted. As mentioned earlier, the current testing of a refractory material is in a gasifier using coal as a feedstock. Additional testing in a gasifier using petroleum coke and mixtures of petroleum coke/coal as feedstock is planned. Petroleum coke may contain higher amounts of vanadium and nickel than coal, which can influence gasifier wear. Until feedback is obtained on the performance of this phosphate containing refractory, no additional research or testing of high chrome oxide refractory materials is planned.

NO/LOW CHROME OXIDE REFRACTORIES

A strategy to develop no/low chrome oxide materials for hot face linings in slagging gasifiers centers on making refractories able to withstand the high temperature gasifier environment and the aggressive corrosive gasifier slags through control of raw materials, brick porosity, and the proper design of the fine and coarse grain microstructure. For purposes of this research, no-chrome refractories contain zero chrome oxide as an addition and low chrome oxide refractories contain less that 30 wt pct chrome oxide. Current research is focused on no-chrome oxide compositions.

Raw material selection for no-chrome oxide refractories is based on engineered material design of the refractory, with selection of the coarse and fine matrix materials using several factors. These factors included information obtained from evaluating major wear mechanisms (corrosive slag and spalling) in high chrome oxide gasifier refractories and the phase diagram data, which acted as a preliminary screening device. Material compatibility, the oxidation/reduction behavior, and the melting temperature were also used to rank potential materials. The relative acidity/basicity of candidate materials was used to give an indication of the ability of materials to withstand corrosive gasifier slags. Material selection was also based on an evaluation of the thermodynamic interactions between slag, gas, and potential refractory materials at the high temperatures used in gasifier operation and on SEM microstructural evaluation of samples exposed to these conditions. Caution must be exercised when using thermodynamic data as it does not indicate reaction kinetics, only what material combinations are thermodynamically stable. Candidate material could appear thermodynamically unstable for use, but may be kinetically stable in practice. Because many promising materials that were identified are not commercially available, the cost, availability, and/or the ability to produce a material were also taken into consideration in selection of candidate materials for gasifier usage.

Both research at Albany and published literature on slagging gasifier refractories[2-6] indicated slag corrosion, reactions between the slag and refractory raw material, and spalling were service limiting issues impacting many materials. Much of the research on refractories for gasifier usage was conducted in the mid 70's to late 80's. Since that time, significant advances have occurred in refractory technology. Between the literature, phase diagrams, thermodynamic data, and other selection criteria; several refractory materials were identified as candidates for possible gasifier use. These materials included Al_2O_3, CaO, MgO, SiO_2, SrO, TiO_2, phosphates, and/or mixtures of them in the coarse and fine grained microstructure.

The sequence of material testing and evaluation was to prepare small "cups" of potential materials or compositions and study interactions between the slag and refractory containment vessel at elevated temperatures.   These small scale cup test samples were made using a fine grained material of the targeted compound, and were approximately 25 mm in diameter and 30 mm in height. Samples had a recession in the top to hold gasifier slag and were heated to 1600^{o}C in an Ar atmosphere for one hour. Interactions between the slag and the test material were evaluated by visual observations (degree of slag/refractory interaction), by slag penetration, and by x-ray crystalline phase identification of new compounds or mineral phases that were created. Slag/refractory interactions indicated by the depth of slag penetration into the crucible are shown in figure 5.

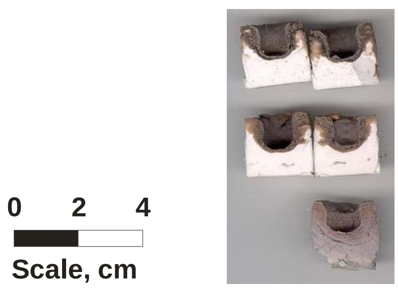

Fig. 5: Cross section of small "cup" tests evaluating refractory/slag interactions at 1600^{o}C in an Ar atmosphere. Different materials are evaluated in the "cup" cut in half to show slag penetration.

Materials identified as having potential from the small scale cup tests were fabricated into larger cups that measured approximately 65 mm in diameter and 65 mm in height. A recession in the cup, similar to that used in the smaller cup tests, held the test gasifier slag. Testing was also conducted using the same conditions as smaller cup samples (1600^{o}C in an Ar atmosphere using a gasifier slag with a one hour soak at the test temperature). The larger cup samples were made using coarse and fine grained matrixes, some with different starting coarse and fine matrix materials. This allowed for the fabrication of test samples with specific targeted material/slag interactions. The goal was to produce an engineered microstructure that would control slag corrosion and penetration. This was done in part by considering particle packing, controlling porosity, and controlling green and fired density. The goal was to engineer a refractory material to resist gasifier slag penetration and corrosion. An example of the larger cup test is shown in figure 6.

Small and large cup tests are a good way to quickly evaluate different materials quickly (over 100 different compositions have been evaluated), but have the drawback that they do not introduce a thermal gradient across a sample. Because gasifier refractories have a thermal gradient, further testing of materials that looked promising are being evaluated in the rotary slag test. This test requires samples measuring 229 mm by 115 mm by 64 mm, a sample size that can also used to evaluate porosity, crushing strength, and creep under load at elevated temperature. Rotary slag testing of a non-chrome oxide refractory and high chrome oxide refractories are shown in figure 7. Testing was conducted for four hours at 1667^{o}C using a gasifier slag feed of 200 grams every 10 minutes and a rotational speed of 1.5 rpm. Refinements are being made to the microstructure of test materials based on rotary slag testing to control grain size and bond matrix materials with the goal of improving slag and wear resistance. Research to develop non-chrome materials for slagging gasifier applications has developed compositions meriting additional research, research that is still on-going.

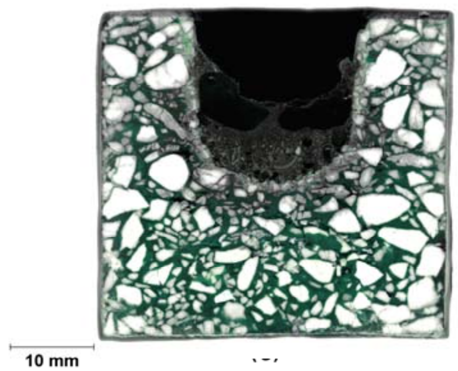

Fig. 6: Cross section of larger cup test sample evaluating slag attack of coarse and fine grained microstructure in Ar at 1600^{o}C.

a. b.

Fig. 7: Refractory samples tested for molten slag resistance in the rotary slag test,
a) samples during rotary slag testing, and b) non-chrome and chrome based refractories after rotary slag testing. Testing was for 4 hours of exposure to a coal gasifier slag at 1667^{o}C.

CONCLUSIONS

The wear of high chromia/alumina refractories used to line the hot face of slagging gasifiers is predominately caused by refractory surface corrosion and spalling. An improved high chrome oxide refractory composition containing phosphates has been patented, produced commercially, and is undergoing field testing in a commercial gasifier. Phosphate containing samples have completed field testing for 17 and 110 days successfully, with continued material evaluation underway. Research and development of gasifier refractory liner materials containing no chrome oxide is underway at Albany. Using information from the literature, phase diagrams, thermodynamic data, and other sources; an improved performance refractory material is being developed in the laboratory. Promising materials are being scaled up from small cup tests to larger cup tests, than to the rotary slag tests to determine potential field test compositions.

REFERENCES

[1]Gasification Markets and Technologies – Present and Future – An Industry Perspective, US DOE/FE Report 0447, US DOE, (July, 2002), pp. 1-53.

[2]W.T. Bakker, "Refractories for Present and Future Electric Power Plants," Key Engineering Materials, Trans Tech Publications, (1993), Vol. 88, pp. 41-70.

[3]Sorell, G., M.J. Humphries, E. Bullock, and M. Van de Voorde, "Material Technology Constraints and Needs in Fossil Fuel Conversion and Upgrading Processes," Int. Metals Reviews, Vol. 31, No. 5, 1986, pp 216-242.

[4]Bakker, W.T., S. Greenberg, M. Trondt, and U. Gerhardus, "Refractory Practice in Slagging Gasifiers," Amer. Ceram. Soc. Bulletin, Vol. 63, No. 7, 1984, pp 870-876.

[5]Bonar, J.A., C.R. Kennedy, and R.B. Swaroop, "Coal-Ash Slag Attack and Corrosion of Refractories," Amer. Ceram. Soc. Bulletin, Vol. 59, No. 4, 1980, pp 473-478.

[6]Starzacher, A.P., "Picrochromite Brick - A Qualified Material for Texaco Slagging Gasifiers," Radex-Rundschau, Vol. 1, 1988, pp. 491-501.

ACKNOWLEDGEMENTS

Support for this research was given by U.S.D.O.E. - Fossil Energy (Gasification Technologies and Advanced Research/Materials) and the Albany Research Center (Advanced Metallurgical Processes).